A STUDY OF THE SEPARATION AND MEASUREMENT OF THE HEAVIER RADIOACTIVE RARE EARTHS

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Abstract of

A Thesis Presented in Partial Fulfillment of the Requirements

for the Degree Master of Science

By

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The Ohio State University

A STUDY OF THE SEPARATION AND MEASUREMENT OF THE HEAVIER RADIOACTIVE RARE EARTHS

JOHN DODGE SERVIS

B. S. A., University of Florida, 1939

Department of Physics

(Approved by M. L. Pool)

In the heavy rare earth region a new radioactive isotope of erbium, Er^{165}, has been produced by proton bombardment of high-purity holmium oxide in the Ohio State University cyclotron. The radiations have been studied by electrometer, magnetic counter, and absorption curve methods, and found to consist of electrons, x, and gamma radiation of a ten-hour half life.

As part of the research, a method for the rapid separation of the yttrium group rare earths through the use of chromatographic elution in a synthetic, cation exchange, resin column with acid ammonium citrate solution and radioactive tracer technique has been developed and described.

Fast neutron bombardment of high-purity samples of terbium oxide have failed to reveal an approximate 3.9-hour half life for the terbium isotopes, Tb^{158} or Tb^{160}.

Verification data have been provided for the radioactive isotopes of holmium as a result of proton bombardment of pure dysprosium oxide and deuteron bombardments of pure holmium oxide.

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A STUDY OF THE EVALUATION AND RELIABILITY OF
THE [illegible] [illegible] RATING

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A STUDY OF THE SEPARATION AND MEASUREMENT OF THE HEAVIER RADIOACTIVE RARE EARTHS

INTRODUCTION

The most desirable target material in cyclotron bombardments is the elemental metal because of its ease of manipulation and inherent purity. Because of the scarcity of chemical methods for the production of rare earth metals, the rare earths necessarily must be bombarded as an oxide. This practice introduces a positron F^{18} activity of 1.8 hours in all bombardments with deuterons and protons. Individual rare earths as furnished by the distributers contain minute quantities of yttrium. This minute quantity of impurity because of large cross section for deuterons and neutrons introduces a negatron Y^{90} activity of 2.6 day half life which largely obscures the remaining rare earth activities. In addition, proton bombardment of yttrium produces a 3.3 day Zr^{89} positron activity which obscures measurements of the rare earths containing this impurity. Also found in the commercial distributors samples are trace amounts of calcium. High cross sections for alpha particles is a characteristic of this impurity. As a result, a 3.92 hour positron, gamma activity of Sc^{44} is formed in the alpha bombardments of the rare earths.

Measurement of rare earth radioactive characteristics thus involves complete purification of individual rare earths prior to,

or immediately after, bombardment. Chemical treatment of the rare earth samples prior to bombardment is attendant with difficulties because of the presence of trace impurities in the chemical reagents commonly used in the laboratory. Thus, while accomplishing purification of the rare earths, the trace impurities of the reagents, when activated, may completely obscure the rare earth sample activity.

The purification by separation of the radioactive rare earth activities after bombardment is considered more satisfactory, since this method lends itself to radiochemical measurement, a much more sensitive method than ordinary chemical technique. A disadvantage of this method is the loss of activity due to chemical treatment and decay of the sample during the time of separation.

This paper, therefore, presents a rapid method for the separation of the rare earths and contaminant activities commonly found in the trace impurities of rare earths supplied by commercial laboratories and, secondarily, extends the knowledge of the radioactive properties of Er^{165}, Tb^{160}, and the holmium isotopes.

HISTORICAL REVIEW

As a result of the radiological safety program of the Manhattan Project (1943-1945), it became necessary to isolate the major fission species in the forms, purities, and amounts necessary for the solution of the radiotoxicological problems inherent in the quantity production of plutonium. In the research that followed, it was found that over thirty of the fission products were members of the rare earth family (isotopes of yttrium and the group lanthanum through europium). The characterization of these rare earths presented very difficult problems that were solved only with the intensification of ion exchange methods originally developed by G. E. Boyd and his coworkers(6) and applied to the rare earth field by Cohn and his coworkers(1). In this paper, Cohn presented the successful separation of the rare earth sequence praseodymium, neodymium, and element 61 (promethium). Continuance of this work at the Clinton Laboratories led to the discovery that most of the ions of zirconium, columbium, cerium, yttrium, barium, strontium, and iodine could be eluted selectively from the organic resins of Boyd by the use of complexing agents, such as ammonium citrate, ammonium oxalate, or ammonium tartrate, under controlled pH conditions(1).

In the meantime, F. H. Spedding and his group at Iowa State College were developing a method for the separation of macro quantities of the rare earths by ion exchange. They reported the satisfactory separation of cerium and yttrium(2); neodymium and praseodymium(3).

HISTORICAL REVIEW

As a result of the radiological safety program of the Manhattan Project (1942-1946), it became necessary to isolate the major fission species in the tracer, milligram, and microgram amounts for the solution of the radiochemical problems inherent in the quantity production of plutonium. In the research that followed, it was found that over thirty of the fission products were members of the rare earth family (isotopes of yttrium and the group lanthanum through europium). The characterization of these rare earths presented very difficult problems that were solved only with the implementation of ion exchange methods originally developed by G. E. Boyd and his co-workers[10] and applied to the rare earths first by Ketelle and his co-workers[11]. In this report, they presented the successful separation of the rare earth elements praseodymium, neodymium, and element 61 (promethium). Development of this work at the Clinton Laboratories led to the successful development of the idea of eluting solutions, various pH values, ionic strengths, and buffer media to elute selectively from the organic resins as found by the use of complexing agents, such as ammonium citrate, ammonium lactate, or ammonium tartrate, under controlled pH conditions[12].

In the meantime, F. H. Spedding and his group at Iowa State College were developing a method for the separation of macro quantities of the rare earths by ion exchange. They reported the satisfactory separation of cerium and yttrium[13], neodymium and praseodymium[14], Later contributions of the Clinton National Laboratory were the separations of several rare earths of the cerium and yttrium groups by ion-exchange resins(5, 6, 7), and the theoretical studies of the reactions of the rare earth complexes(8, 9, 10). This led to further modification of ion-exchange technique of shorter columns and more rapid separation rates(11, 12).

These developments enabled Hicks and Wilkinson(13, 14, 15, 16) at the Crocker Radiation Laboratory of the University of California to institute cyclotron bombardments of the rare earth elements with confidence in the speed and certainty of chemical identification. They were able to make a series of studies of the neutron-deficient, radioactive isotopes of neodymium, promethium, terbium, holmium, thulium, hafnium, tantalum, and rhenium through the use of ion-exchange separations, following cyclotron bombardments employing helium ions, deuterons, protons, or fast neutrons. Latest developments at the same laboratory have been the characterization of the neutron-deficient, radioactive isotopes of cerium, praseodymium, and neodymium(17).

Hicks and Wilkinson(13) in their series of studies bombarded very pure dysprosium oxide with 38 Mev alpha particles, and the rare earth elements were subsequently chemically separated by the ion-exchange, resin-column method. The erbium fraction was found to contain an activity whose decay gave a half life of approximately 11 hours. Absorption measurements showed the radiations to consist mainly of electromagnetic radiations corresponding to the average

energies of holmium L and K x-radiation 7.2 and 52 Kev, respectively; hard gamma radiation of 1.1 Mev energy; and very soft electrons of total range approximating 10 mg/cm^2 aluminum in very low yield. Since no 11-hour activity was detected in the column separated erbium fraction from holmium bombarded with 19 Mev deuterons, allocation of the 11-hour activity was made to Er^{163}. No proton bombardments of holmium were mentioned in this study.

Also included in their series of studies were the neutron-deficient, radioactive isotopes of holmium which were produced by alpha-particle bombardment of terbium and by proton and deuteron bombardment of dysprosium. They reported a 34-minute, a 4.6-hour, a 5.2-day, and a 65-day activity as a result of dysprosium bombardment with protons. The allocation of the 22.5-minute, 4.6-hour, and 65-day holmium activities to masses 160, 161, and 162, respectively, was made on the basis of yields in bombardments of terbium with 38, 30, and 19 Mev alpha particles. The 5.2-day activity was allocated to mass 163, since it was not observed in alpha-particle bombardments of terbium, or in fast-neutron bombardments of holmium, but was formed in yields approximately the same as the other isotopes in proton bombardments of dysprosium.

Butement(18) has recently reported a 10 Mev proton bombardment of holmium oxide of over 99.97% purity and a resulting activity in the erbium fraction which consisted solely of electromagnetic radiation with a half life of 10 ± 0.1 hour. This was measured as

holmium X-rays, and the activity was, therefore, attributed to K capture in Er^{165}, formed in the reaction

$$Ho^{165}\ (p,n)\ Er^{165}.$$

EXPERIMENTAL

Bombardments

In most cases, ten to twenty-five milligram samples of the rare earth oxides were bombarded in aluminum interceptor targets placed in the beam of the Ohio State University cyclotron. The finely powdered oxide was placed in the well of the target, heated to a temperature of 500 degrees Centigrade, and then lightly pressed prior to bombardments. Targets were covered with .0035-inch aluminum foil just before target mounting. Bombardments were made with 7.4 Mev protons, 10 Mev deuterons, and 20 Mev fast neutrons for periods ranging from five minutes to seven hours.

Fast-neutron bombardments were made on twenty-five milligram samples of the oxides in small plastic capsules. The capsule was placed in a copper target mounted behind a copper target well, containing lithium. The target assembly was then placed in the beam of 10 Mev deuterons and the fast neutrons obtained from the Li (d,n) Be reaction. In this type of bombardment, it was necessary to include a capsule without sample in order to determine the capsule activity in itself.

Column Separation

Principles of Column Separation

One of the most difficult processes in the field of chemis-

try has been the separation of the rare earths from each other into their pure states. Their chemical and physical properties are so similar that a single operation only enriches one component. Since 1945, a number of research workers have reported studies on the application of chromatographic and ion-exchange methods to the separation of the rare earths(1, 2, 3, 4, 5, 6, 8, 9). Most successful rare earth separations of those reported involved the adsorption of rare earths on organic resins and subsequent elution with complexing agents, such as citric acid-ammonium citrate solution at controlled pH. The marked success of the processes described depends on the fact that the rare earths form complexes with the citrate ions. If the pH is suitably adjusted, competition is set up for the rare earth ions between the citrate complexes and the active centers of the resin. As the citrate solution washes the rare earths down the column, each rare earth ion is adsorbed and desorbed many times. The variance of equilibrium constants of the rare earths-citrate complexes accounts for the difference in the rate of travel down the column and thus leads to their separation.

The problem of separation then becomes one of moving one of the rare earth cations out of a narrow adsorption band at the top of the column at a more rapid rate than the others, so that most of it reaches the bottom of the column before much of the second does. Attaining optimum separations involves the use of an eluting agent which will preferentially remove one component with minimum movement of the others down the column. The reactions concerned in complex

elution of rare earths may be considered as reactions of a cation A^{+++} adsorbed on a resin column. When an ammonium citrate solution, at a pH which will barely support the formation of a complex ion, is passed through the column, NH_4^+ in the solution exchanges with A^{+++} on the resin in accordance with the following reversible reaction:

$$3NH_4^+ + A^{+++}(\text{resin}) \longleftrightarrow A^{+++} + 3NH_4^+(\text{resin}) \qquad (1)$$

The cation then enters into the further equilibrium:

$$A^{+++} + (\text{citrate ion})^{\equiv} \longleftrightarrow A\ \text{citrate} \qquad (2)$$

The fraction of total A^{+++} found in the citrate complex is determined by the relative equilibrium constants of Reactions (1) and (2).

The exchange reactions (1) take place a certain number of times in each unit length of column. Therefore, the closer the approach to equilibrium conditions, the greater the number of theoretical plates and degree of separation. Improvement in separation involves the finding of conditions which lend themselves to the most rapid attainment of equilibrium conditions under the practical considerations of operation. The setting of optimum conditions is essentially a balancing of the desire for longer columns, slower flow rates, finer resin particles, and small cation-to-resin ratio against the desire for high yield and speed.

Combined with the data of Ketelle and Boyd(6), the results of this research indicate a relative adsorbability of the rare earths

Gd > Tb > Dy > Y > Ho > Er > Tm > Yb > Lu

This progression is in the same order as that of the crystal ionic radii.

Owing to the very close similarity of yttrium, dysprosium, and holmium, the triad Dy, Y, and Ho constitutes what may be taken as the most difficultly separable of all the rare earths. The yttrium subgroup of the rare earths of terbium through lutecium corresponds to the filling in of the second seven electrons in the 4f shell of the atom, and a maximum similarity in both the relative radii and adsorbability is found with Yb and Lu. Examination of the data of Ketelle and Boyd(6) and the relative ionic radii of Bommer indicates that cerium and praseodymium are the easiest to separate; and ytterbium and lutecium are the most difficult, excepting for the separation of the quasi rare earths yttrium and dysprosium.

Rapid column separations necessary for the characterization of short-lived activities in the region of dysprosium, holmium, and erbium, therefore, only constitute an enrichment of one component in the presence of the other activities. Yttrium with its high activities becomes the limiting factor in the speed of elution.

Operation of the Column

Column separations were made using Dowex 50(7), a synthetic cation exchange resin containing nuclear sulfonic acid groups as the sole ion-active group at any pH value. The resin was obtained from the laboratories of the Dow Chemical Company and was supplied

in the sodium form of colloidal dimensions. This material had a density of 1.5 gm/ml in the dry form and an effective molecular weight of 168.

The preparation of the resin prior to use consisted of heating the material to 100°F. with 1-1/2 volumes of 4M ammonium chloride, cooling, and decantation through three cycles. This action was followed by eight washings with 2-1/2 volumes of distilled water. After each wash, the supernatant and any fine material in it was discarded.

The eluting agent employed was 0.25 molar citric acid, accurately adjusted to a pH 3.05 with ammonium hydroxide and protected against mold growth with 1/2% phenol solution.

The column consisted of a thin polystyrene tube, 0.3 centimeter in thickness, 1.4 centimeter in internal diameter, and 20 centimeter in length. The utilization of a polystyrene column in place of a longer glass column, mentioned in the literature, permitted a more efficient survey of the movement of the radioactive rare earths through the column. The resin bed was 15 centimeter in length and was supported on a filter of glass wool.

The column apparatus (Figure 1B) consisted of the resin bed (A), plastic column (B), and the flow-rate bottle which controls the rate of flow through the adjustment of hydrostatic head (C). The flow rate was adjusted to 0.25 ml/cm^2 of column area/minute. This flow rate corresponded to six drops per minute.

The first step in operation after removing the rare earth in the sodium form of colloidal dimensions. This material had a density of 1.5 g/ml in the Na form and an effective molecular weight of 10⁵.

The preparation of the resin prior to use consisted of washing the material in water, with 2-1/2 volumes of 1N ammonium chloride, washing, and decantation through three cycles. This cycle was followed by eight washings with 2-1/2 volumes of distilled water. After each wash, the supernatant and any fine material in it was discarded.

The eluting agent employed was 0.15 molar citric acid, accurately adjusted to a pH 3.10 with ammonium hydroxide and preserved against mold growth with 1.0% phenol solution.

The column consisted of a thin polystyrene tube, 0.9 centimeter in thickness, 1.1 centimeter in internal diameter, and 80 centimeters in length. The utilization of a polystyrene column in place of a longer glass column, mentioned in the literature, permitted a more efficient survey of the movement of the radioactive rare earths through the column. The resin bed was 15 centimeters in length and was supported on a filter of glass wool.

The column apparatus (Figure 13), consisted of the resin bed (1), plastic column (2), and the flowmeter bottle which controls the rate of flow through the adjustment of hydrostatic head (3). The flow rate was adjusted to 0.37 ml/cm² of column area/minute. This flow rate corresponded to one drop per minute.

The first step in operation after preparing the resin was oxides from the aluminum target was to dissolve this material in a minimum of concentrated nitric acid, precipitate the hydroxides with concentrated ammonium hydroxide, centrifuge the solution, decant the supernatant liquid, and wash the precipitate. This process is repeated several times and the precipitate finally dissolved in nitric acid. The rare earth fluorides are precipitated by the addition of 5 cc concentrated HF. These are removed by centrifugation and washed with distilled water. At this point, the contaminating activities are limited to the rare earths and scandium. The fluorides are then dissolved in a nitric acid-boric acid solution (8-10$\underline{M}$ HNO_3 saturated with boric acid), and the complete cycle of purification is repeated again. The final hydroxides are dissolved in HCl, pH 1-1.5, and transferred to the top of the ion-exchange resin column.

This starting solution was first slowly passed through the column, causing the solute mixture to be adsorbed at the top. The eluting solution was then passed through the column at the specified rate, the effluent being monitored by means of a special apparatus consisting of a mica-windowed, Geiger-Muller tube mounted in a lead shield 0.5 inch in thickness on the sides and 0.25 on the end facing the column. A 0.33-inch opening in the end plate was provided for scanning the effluent. The tube was attached to a counting rate meter and Esterline-Angus recorder. By this means, it was possible to obtain a continuous record of the beta and gamma emitters in the effluent of the column. Fractions of the effluent were collected at

definite changes in activity and fractions containing more than twice background activity were transferred to evaporation dishes, evaporated, and ignited to 1400 degrees Fahrenheit in the electric furnace. The rare earth residue was then extracted with hot nitric acid and the hydroxide precipitated with ammonium hydroxide and dried under an infra-red lamp.

Results in Column Separation

Several preliminary runs were made with various types and mesh-size, ion-exchange material in an effort to determine optimum flow rates, column lengths, and mesh size. The first preliminary run was made with a 50 cm x 1 cm, Dowex 50, 60-mesh size column with a flow rate of 0.03 ml/cm^2/minute and a pH 3.05 ammonium citrate solution at room temperature$^{(13)}$. This experimental separation was found to be unsatisfactory from the time and completeness of separation viewpoint. First activity appearance occurred in the terms of days and little differentiation was noted.

The second experimental run was made with a 90 cm x 1/2 cm Ionex, 150-300-mesh size column with a flow rate of 1.0 ml/cm^2/minute and a pH 3.05 ammonium citrate solution at a temperature of 100 degrees Centigrade$^{(6)}$. This method was also considered unsatisfactory from the time and operational viewpoint, but separation of yttrium and zirconium was accomplished. This separation required thirty-six hours, but survey scanning of the column indicated the

feasibility of using a much shorter column. Examination of the scanning plot (Figure 1) indicated that satisfactory separation could have been obtained with a 15-cm column in one-third of the time. Bubble formation in the bed of column due to the elevated temperature indicated the need for room-temperature operation.

During the first preliminary experiments, it had been noted that the rate of initial movement of the activities down the column was proportional to the initial adsorption technique. When initial adsorption occurred with ion-exchange material outside of the column, as recommended by Hicks(13), slow elution and separation occurred. When initial adsorption was made in the upper-bed levels by the method of Tompkins(12), rapid elution was obtained.

The third experimental run results are shown in Figure 2, with the equipment and method previously described and illustrated in the Appendix. This curve represents the time at which the four groups of activities, resultant from the four-hour deuteron bombardment of 20 mg of terbium oxalate, 20 mg of holmium oxalate, and 20 mg of thulium chloride, eluted by ammonium citrate, passed the scanning tube and illustrates the degree of separation obtained. Yttrium found in the plot is the common contaminant of the three materials. This experiment reveals a rapid method of separation but could be improved upon to give more specific separation of the individual rare earths by decreasing the flow rate by one-half.

Radioactive Measurements

After separation and recovery of the individual rare earth hydroxides, the samples were mounted on small cardboard "drug boxes" and covered with 0.002-inch Zapon. Radiation characteristics were determined by means of lead, copper, and aluminum absorptions of the radiations, and by half-life decay curves. Aluminum absorptions were taken in the accepted manner, and the energy of beta particles was determined from the range of electrons in aluminum. This range has been taken as the minimum absorber thickness required for total absorption. Lead absorptions were utilised to determine the radiation half thickness in gm/cm^2. From this half thickness measurement, relative gamma-ray energies could be determined. Aluminum and copper absorptions were used to determine X-ray half thickness, absorption coefficients, and wave lengths.

Measurements were made with end-on, Geiger-Muller tube counters which had 3 mg/cm^2 mica windows and were filled with 10 cm argon and 1.0 cm alochol. Variations in counter efficiency were taken into account by the use of a cobalt standard. The scaling circuit used was the conventional type, scale of 64. A crude beta-ray spectrometer of low resolution enabled the distinction of positive and negative electrons.

Measurements were also made with a Wulf, unifiliar electrometer, an ionization chamber containing freon gas under twenty atmospheres' pressure. Radiations entered the ionization chamber

through an aluminum foil of 20 mg/cm^2. Directly over the electrometer was an electromagnet arrangement by which charged particles could be deflected away from the ionization chamber and electromagnetic radiations alone measured. Gamma radiation decays were measured by insertion of 1/4 inch of aluminum between activated sample and ion chamber.

Holmium Isotopes

In an effort to verify the activities of the radioactive isotopes of holmium, short and long bombardments of dysprosium oxide with protons were coupled with deuteron bombardments of holmium. The literature to date lists six known, radioactive isotopes(15, 20) as listed on the following page, and one stable isotope 100% pure Ho^{165}.

The first experimental bombardment was a 10 Mev deuteron bombardment of 85-minute duration on a sample of holmium oxide prepared by Dr. J. K. Marsh of Oxford for Adam Hilger, Ltd., Laboratory No. 12425. This sample was considered to be remarkably pure for holmium, as it contained 2% dysprosium and only traces of yttrium, calcium, and magnesium.

Measurement of the resultant total activity through eight half lives on the Wulf electrometer revealed a 27-hour half life consisting of a 1.75 Mev B^- particle, and a .95 Mev gamma ray (Figure 6). This is in agreement with values previously mentioned. Electromagnetic radiation decay was in accord with that of the total

Six Known Radioactive Isotopes

Isotope	Produced By	Type of Radiation	Half Life	Energy of Radiation	
				Particles Mev	Gamma Ray Mev
1. Ho^{160}	Tb-α-3n	K, e^-, B^+	22 min.	0.17 (e^-) 1.3 (B^+)	1.2
2. Ho^{161}	Tb-α-2n Dy-p-n Dy-d-2n	K, e^-, γ	4.6 hr.	0.1 (e^-)	1.1
3. Ho^{162}	Tb-α-n Dy-p-n Dy-d-n 2n	K, B^-, e^-, γ	65 days	0.1 (e^-) 0.8 (B^-)	1
4. Ho^{163}	Dy-p-n Dy-d-n 2n	K, e^-, γ	5.2 days 7 days	 0.4	0.5 1.2
5. Ho^{164}	Ho-γ-n Dy-p-n Ho-n-2n	B^-	34 min. 47 min.	0.95 0.7	
6. Ho^{166}	Ho-n-γ	B^-, γ	27 hr. 30 hr.	1.8 1.88 1.64	0.8 1.36

activity measured. The reaction predominant in the bombardment was Ho^{165} (d,p) Ho^{166}. No visible evidence of an Ho^{165} (d,2n) Er^{165} reaction could be noted.

The second experimental bombardment was a 7.4 Mev proton bombardment of 20-minute duration of a sample of dysprosium oxide prepared by Dr. Prandtl of Munich for Adam Hilger, Ltd., Laboratory No. 6402. This sample was of extreme purity as it contained only traces of calcium, gadolinium, and praseodymium.

Measurement of the total activity through nine half lives on the Wulf electrometer revealed a complex decay curve which, upon analysis, indicated three activities of 19 minutes, 39 minutes, and 1.8 hours. Absorption and magnetic counter measurements indicated the 1.8-hour activity as F^{18} produced by the O^{18} (p,n) F^{18} reaction. The 19-minute and 39-minute activities correspond to the listed activities of Ho^{160} and Ho^{164}.

The third bombardment was a 7.4 Mev proton bombardment of four hours' duration of the sample of the second bombardment. Measurement of the total activity through eight half lives with the electrometer revealed a complex decay curve that indicated three activities of 4 hours, 18 hours, and 7 days (Figure 4). Absorption and electromagnetic radiation decay curves indicated these activities to be x and gamma radiation. The 4-hour activity corresponds to Ho^{161} and the 7-day activity to Ho^{163}. The 18-hour activity is not reported in the literature and may be due to the presence of gadolinium.

Terbium Isotopes

The literature of Hevesy, Levi, and others[19] has reported a 3.9-hour activity in the isotope of terbium of mass number 160. This activity has been formed by a Tb^{159} (n,γ) Tb^{160} reaction. To substantiate this activity, a sample of column-separated terbium was obtained from the Oak Ridge National Laboratory. This sample was as pure as present chemical techniques can provide and was bombarded with fast neutrons for a period of four hours at an intensity of 20 Mev. Measurements of the resultant activity of capsule plus sample and capsule alone (Figure 7) gave no indication of a 3.9-hour activity as a result of either fast- or slow-neutron bombardment.

Erbium Isotopes

The Bureau of Standards[20] lists six stable isotopes of erbium of mass number 162, 164, 166, 167, 168, and 170; and two radioactive isotopes of mass number 160 and 171 with half lives of 9.4 days and 7.5 hours, respectively. To date, there is no listing for the mass number 165, although examination of the isotope tables at higher and lower atomic numbers indicates the good probability of a radioactive isotope of moderate half life that decays by electromagnetic radiation being existent at this number.

To develop this thought, a series of bombardments was undertaken. A first experiment consisted of the deuteron bombard-

ment and measurement of Hilger Sample No. 12425, mentioned under holmium isotopes. No new activity was observed in this activation as the Ho^{166} activity was predominant. This finding is in agreement with that of Hicks and Wilkinson(16).

The second step was the bombardment of Sample No. 12425 with 7.4 Mev protons for a period of four hours. Scalar, magnetic electrometer and absorption measurements through seven half lives revealed a new electromaganetic radiation decay half life of ten hours that corresponded to x and gamma radiation accompanied by a weak electron emission (Figure10). Thin aluminum absorption pictured an electron end point corresponding to 50 mg/cm^2 or 0.22 Mev energy. Lead absorption data gave a half thickness of 7600 mg/cm^2, which, when corrected, corresponds to a gamma energy of 0.65 Mev (Figure11). The activation of impurities was indicated by the presence of long decay periods in the electron and gamma decays.

A third step in the development was the six-hour proton bombardment of a sample of column-separated holmium oxide obtained from the Oak Ridge National Laboratory. Although of extreme purity, only thirteen milligrams were available, and, consequently, limited the amount of activity available for absorption measurements. Exact purity of the sample was unknown and thus gave rise to doubt as to the identification of the longer half-life activity present in the sample after the expiration of the ten-hour electron, ments and measurement of Silver Sample No. 14217, continued under helium leakage. No new activity was observed in this calibration as the Ag^{108} activity was predominant. This finding is in agreement with that of [illegible] and [illegible][24].

The second step was the bombardment of Sample No. 17415 with 1.4 Mev protons for a period of four hours. Geiger, magnetic electrometer and absorption measurements through [illegible] revealed a new electroscopic radiation decay half life of [illegible] hours that corresponded to x and gamma radiation accompanied by a weak electron emission (Figure 10). This aluminum absorption plotted an electron end point corresponding to 30 mg/cm^2 or 0.18 Mev energy. Lead absorption data gave a half thickness of 7000 mg/cm^2, which, when corrected, corresponds to a gamma energy of 0.85 Mev (Figure 11). The evaluation of absorption was inhibited by the presence of long decay periods in the electron and gamma decay.

A third step in the development was the cyclotron proton bombardment of a sample of enriched-separated isotope oxide obtained from the Oak Ridge National Laboratory. Although of extreme purity, only thirteen milligrams were available, and, consequently, limited the amount of activity available for absorption measurements. Exact purity of the sample was unknown and thus gave rise to doubt as to the identification of the longer half-life activity present in the sample after the extraction of the [illegible] element.

x, and gamma radiation were in agreement with the findings of the second experiment. Thin aluminum absorption measurement gave an electron end point of 50 mg/cm^2 (Figure 12). Lead absorption measurements were inconclusive because of the weak intensity of radiation. The ratio of the intensity of the ionization by the beta rays to that by the gamma rays was approximately 10 to 1, which corresponds to an emission of about ten gamma rays per electron.

n. and gamma radiation were in agreement with the findings of the second experiment. This situation throughout the experiment gave an [illegible] and [illegible] at 20 [illegible] (Figure 12). [illegible] measurements were inconclusive because of the weak intensity of radiation. The ratio of the intensity of the [illegible] to the beta rays to that for the gamma rays was approximately 10 to 11 which corresponds to an emission of about two gamma rays per electron.

CONCLUSIONS AND SUMMARY

1. Rare earth ions can be separated from one another through the use of ion-exchange columns, but complete separation of these ions cannot be accomplished in less than twelve hours. This method of chromatographic elution in a Dowex 50, ion-exchange column can be adapted to remove contaminating activities other than the rare earths and to separate the lighter and heavier rare earths in less than twelve hours.

Refinement of the factors of separation (flow rate, elution solution, and column length) can lead to complete separation of rare earths as target materials prior to bombardment.

2. Some of the radioactive isotopes of holmium have been measured and activities found that correspond to the 20-minute half life of Mass No. 160; 4.6-hour half life of Mass No. 161; 7-day half life of Mass No. 163; 39-minute half life of Mass No. 164; and 27-hour half life that corresponds to Mass No. 166.

3. The stable isotope of terbium has been bombarded with neutrons in an effort to determine the presence of a 3.9-hour half life in the terbium isotope of Mass No. 160. No comparable activity, as mentioned in the literature(19), could be distinguished. The conclusion is that no 3.9-hour activity exists in the isotopes of Tb^{158} or Tb^{160}.

4. A new radioactive isotope of erbium has been found from the proton bombardment of high-purity samples of holmium oxide. This radioactive isotope Er^{165} decays by electron, x, and gamma radiation with a ten-hour half life and electron energy of 0.22 Mev.

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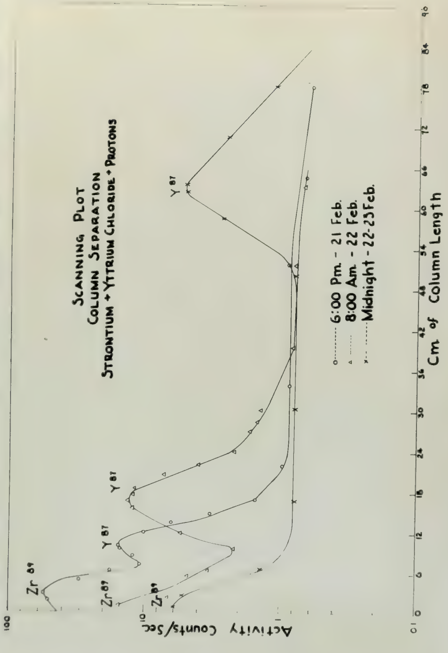
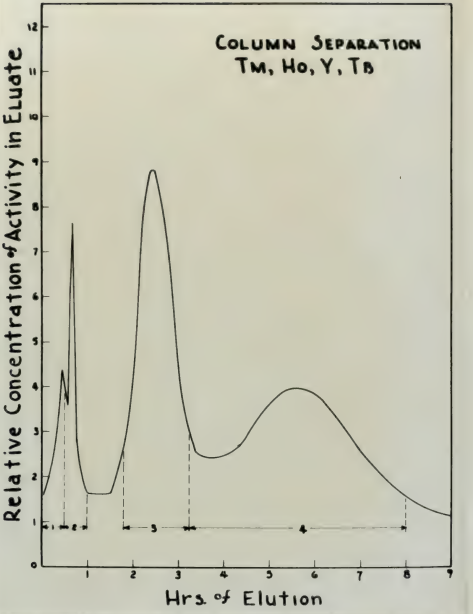
APPENDIX

FIGURE 1



Scanning Plot
Column Separation
Strontium + Yttrium Chloride + Protons

FIGURE 2



COLUMN SEPARATION
TM, HO, Y, TB
Relative Concentration of Activity in Eluate
0
1
2
3
4
5
6
7
8
9
10
11
12
1
2
3
4
5
6
7
8
9
Hrs. of Elution
1
2
3
4

FIGURE 3

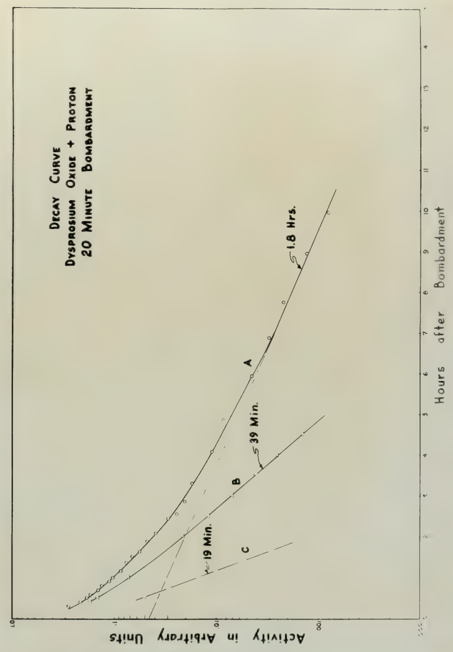

DECAY CURVE
DYSPROSIUM OXIDE + PROTON
20 MINUTE BOMBARDMENT
A
1.8 Hrs.
B
39 Min.
C
19 Min.
Activity in Arbitrary Units
1.0
10
100
Hours after Bombardment
1
2
3
4
5
6
7
8
9
10
11
12
13
14

FIGURE 4

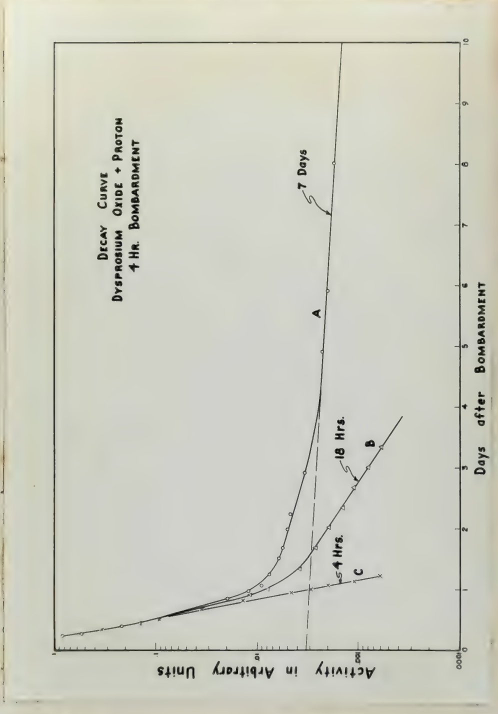

Decay Curve
Dysprosium Oxide + Proton
4 Hr. Bombardment
7 Days
A
18 Hrs.
B
4 Hrs.
C
Days after Bombardment
0
1
2
3
4
5
6
7
8
9
10
Activity in Arbitrary Units
1
10
100
1000

FIGURE 5

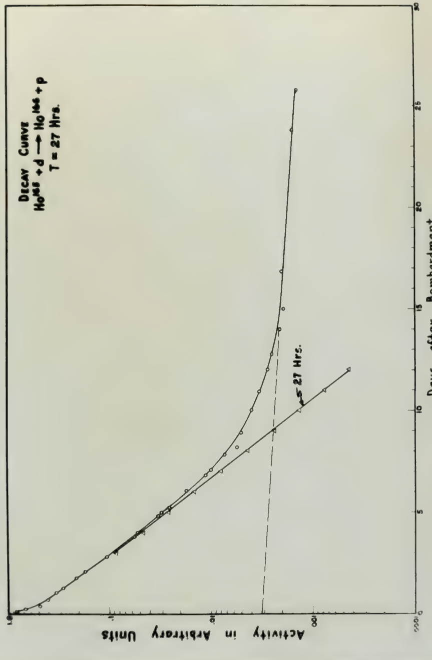

DECAY CURVE
$Ho^{165} + d \longrightarrow Ho^{166} + p$
T = 27 Hrs.
27 Hrs.
Activity in Arbitrary Units
1.0
.1
.01
.001
.0001
Days after Bombardment
0
5
10
15
20
25
30

FIGURE 6

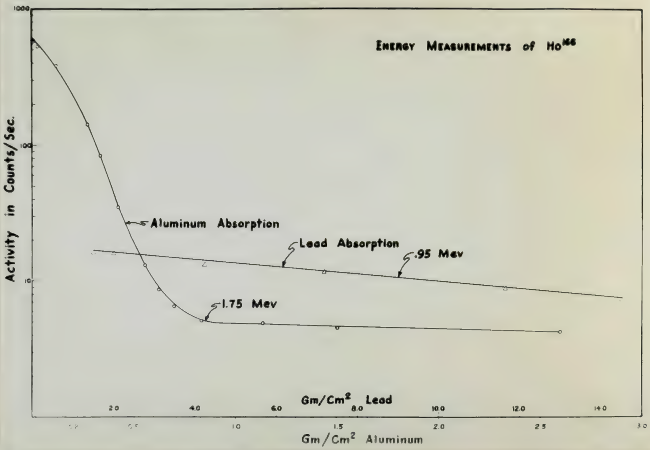

ENERGY MEASUREMENTS of Ho^{166}
Activity in Counts/Sec.
1000
100
10
Aluminum Absorption
Lead Absorption
.95 Mev
1.75 Mev
Gm/Cm^2 Lead
2.0
4.0
6.0
8.0
10.0
12.0
14.0
0.5
1.0
1.5
2.0
2.5
3.0
Gm/Cm^2 Aluminum

FIGURE 7

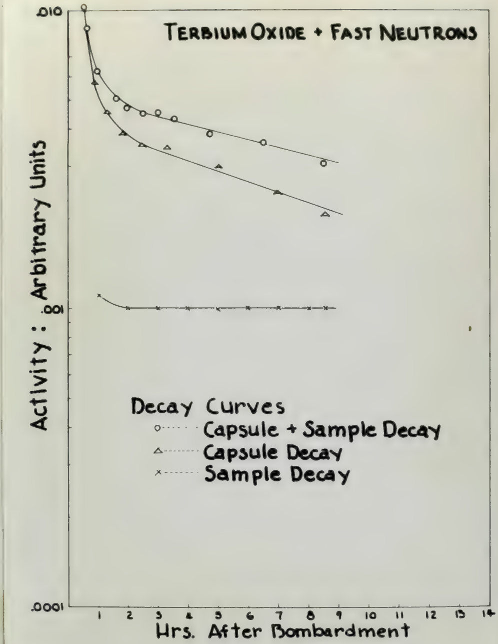

TERBIUM OXIDE + FAST NEUTRONS
.010
.001
.0001
Activity : Arbitrary Units
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Hrs. After Bombardment
Decay Curves
Capsule + Sample Decay
Capsule Decay
Sample Decay

FIGURE 8

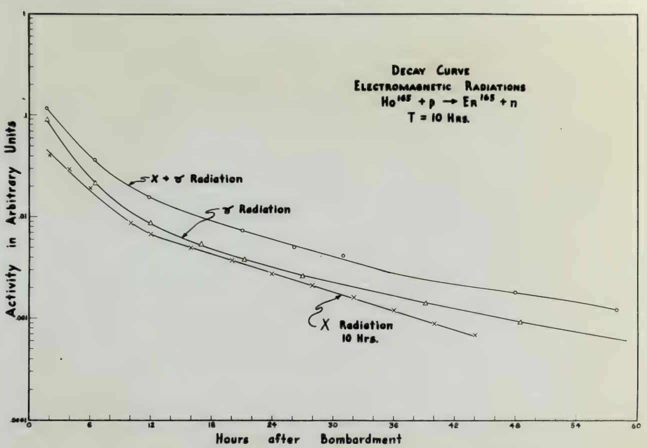

DECAY CURVE
ELECTROMAGNETIC RADIATIONS
$Ho^{165} + p \rightarrow Er^{165} + n$
T = 10 HRS.
X + γ Radiation
γ Radiation
X Radiation
10 Hrs.
Activity in Arbitrary Units
1
.1
.01
.001
.0001
0
6
12
18
24
30
36
42
48
54
60
Hours after Bombardment

FIGURE 9

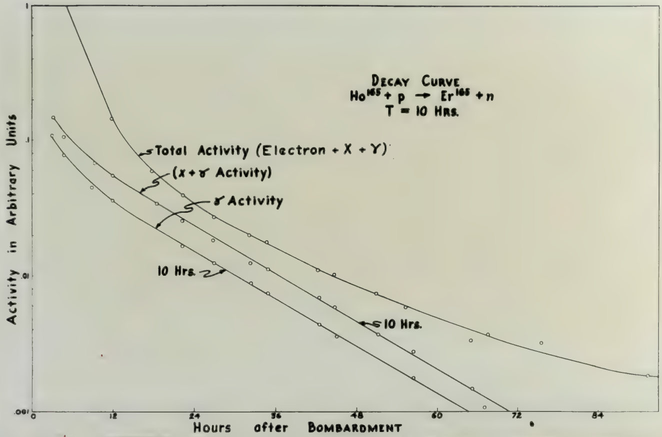

DECAY CURVE
$Ho^{165} + p \rightarrow Er^{165} + n$
T = 10 HRS.
Total Activity (Electron + X + Y)
(X + γ Activity)
γ Activity
10 Hrs.
10 Hrs.
Activity in Arbitrary Units
1
.1
.01
.001
0
12
24
36
48
60
72
84
Hours after BOMBARDMENT

FIGURE 10

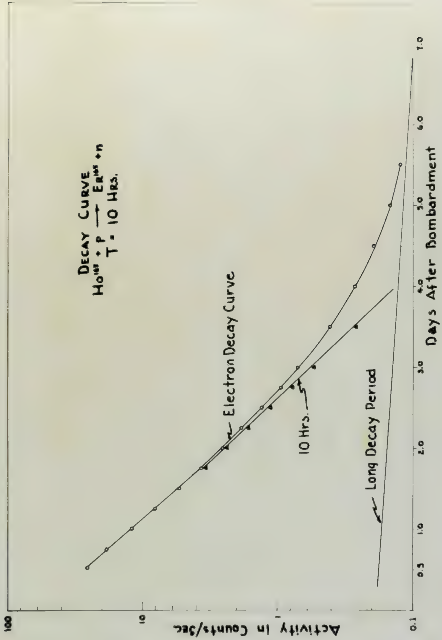
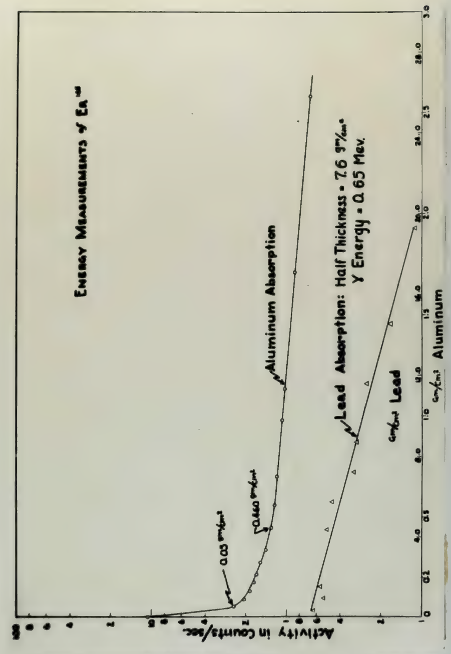
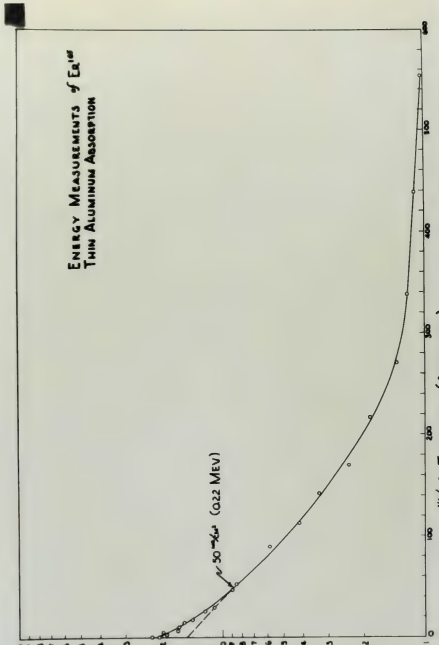

Decay Curve
$Ho^{165} + p \longrightarrow Er^{165} + n$
T = 10 Hrs.
Electron Decay Curve
10 Hrs.
Long Decay Period
Activity in Counts/Sec.
100
10
1
0.1
Days After Bombardment
0.5
1.0
2.0
3.0
4.0
5.0
6.0
7.0

FIGURE 11


Energy Measurements of Er169
Aluminum Absorption
Lead Absorption: Half Thickness = 7.6 gm/cm²
Y Energy = 0.65 Mev.
0.05 gm/cm²
0.460 gm/cm²
Activity in Counts/sec.
gm/cm² Lead
gm/cm² Aluminum
100
8
6
4
2
10
8
6
4
2
1
8
6
4
2
1
0
0.2
4.0
0.5
8.0
1.0
12.0
1.5
16.0
2.0
20.0
24.0
2.5
28.0
3.0

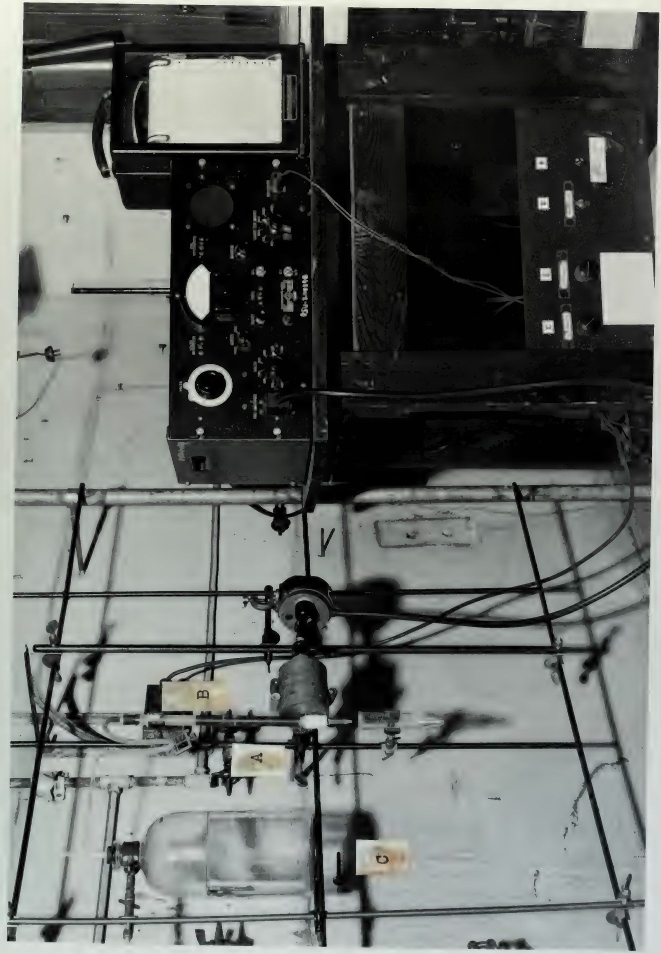
[illegible]

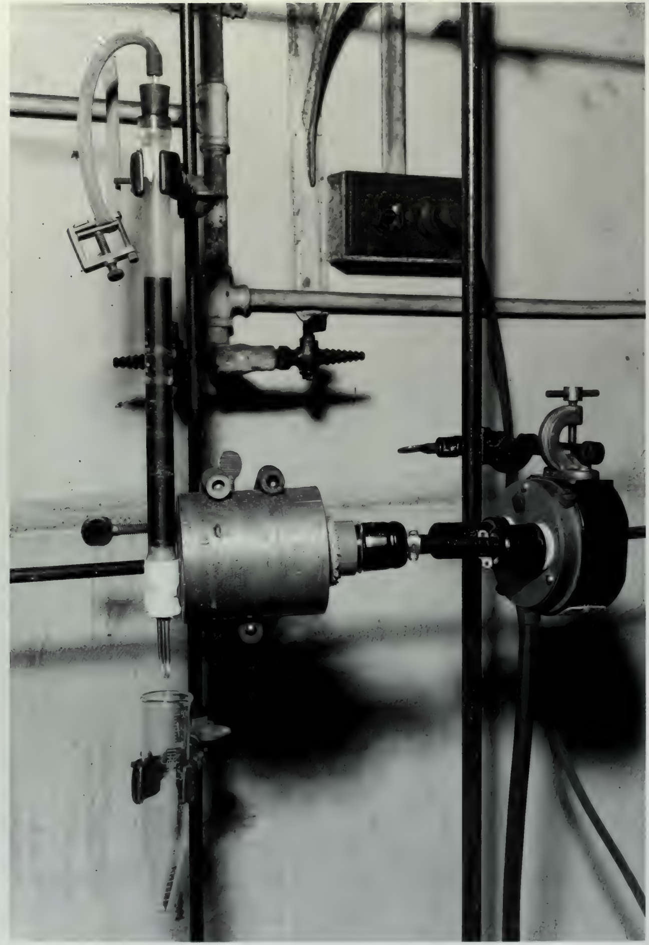
FIGURE 12


ENERGY MEASUREMENTS of ER^{169}
THIN ALUMINUM ABSORPTION
50 mg/cm² (0.22 MEV)
ACTIVITY IN COUNTS/SEC.
mg/cm² THICKNESS (ALUMINUM)
0
100
200
300
400
500
600
1
2
3
4
5
6
7
8
9
10
2
3
4
5
6
7
8
9
100

[illegible]

FIGURE 13





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